

THERMOPLASTIC RESIN COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a thermoplastic resin composition
5 capable for being used for skin materials of automotive interior parts due to
excellent extrusion and calender moldability. More particularly, it relates to an
olefin-based thermoplastic resin composition comprising a base composition
comprising a polypropylene resin, an olefin copolymer rubber, a processing oil,
and a low-density polyethylene resin or a high-density polyethylene resin;
10 organic peroxide crosslinking agent; a crosslinking aid; and
polytetrafluoroethylene resin.

BACKGROUND OF THE INVENTION

Polyvinylchlorides (PVCs) or PVC/acrylonitrile-butadiene-styrene graft
15 copolymer(ABS) alloy extruded sheets or calendered sheets have been widely
used for skin materials of automotive interior parts such as instrument panel,
door trim panel, headlining, and the like. Recently olefin-containing
thermoplastic polyolefin (TPO) sheets have replaced PVCs which have a few
drawbacks such as the difficulty in recycling and lightening, generation of
20 environmentally unfriendly compounds, fogging phenomenon, and offensive
odor. However, since a processing oil is added to assist the molding process of
olefin copolymer rubbers such as ethylene-propylene-diene monomer (EPDM),
the olefin-containing thermoplastic elastomer resins have poor calender
moldability and a low melt strength which cause deterioration in the second
25 moldability such as vacuum thermoforming, thus being inappropriate to use as
automotive parts requiring deep drawing. When an amount of the processing
oil used is reduced and a degree of crosslinking of EPDM is increased to
improve the calender moldability, the molded articles have a very rough
surface. On the other hand, if the degree of crosslinking of EPDM is lowered,

the obtained resin composition sticks to the surface of rolls at the time of molding process.

To solve such problems, US Patent No. 4,212,787 discloses that pre-crosslinked EPDM rubber is diluted into a polypropylene resin having good fluidity. However, practically sufficient elasticity and mechanical properties cannot be obtained to use for complicated articles such as instrument panel and door trim panel because the level of crosslink density is low. Further, it requires special facilities for crosslinking process and dilution process and the manufacturing cost is also increased. JP Unexamined Publication No. 48-26835 discloses that a polypropylene resin and EPDM rubber are pre-mixed and melt-kneaded and then it is heat-treated with peroxide. However, practically sufficient degree of crosslinking and viscosity to use for calender molding cannot be obtained due to hyper-degradation of the polypropylene resin and local crosslinking of EPDM rubber. US Patent No. 4,311,628 discloses a method of homogeneous crosslinking of EPDM rubber using a phenol-base crosslinking agent. The resin prepared by this method exhibits better elasticity and mechanical properties due to favorable degree of crosslinking and homogeneous particles compared to the resin prepared by using peroxide-base crosslinking agent but there are drawbacks in that there are problems associated with prolonged crosslinking time, use of an expensive crosslinking agent raises the cost of final products, and the resin has poor solubility, resulting in decrease of coatability. Further, US Patent No. 4,212,787 discloses a peroxide-non-curable-hydrocarbon rubbery material such as polyisobutylene (PIB) and butyl rubber (BR) is used when EPDM/polypropylene composition is cured and kneaded with peroxide to improve the fluidity without degrading properties of the thermoplastic elastomer composition. However, even if the thermoplastic elastomer composition exhibits homogeneous crosslink density of EPDM, the crosslink density of the final products are not sufficient for calender molding. Therefore, the composition is poor in mechanical strength,

moldability, permanent compression set and heat resistance.

SUMMARY OF THE INVENTION

In order to solve the above problems, we developed a novel olefin-base
5 thermoplastic resin composition that maintains the crosslink density of an
olefin copolymer rubber. This is accomplished in part by adding an organic
peroxide crosslinking agent, a crosslinking aid, low density or high density
polyethylene resin, and polytetrafluoroethylene (PTFE) in an appropriate
amount during the crosslinking process of a blend of a polypropylene resin, an
10 olefin copolymer rubber and a processing oil.

Accordingly, an object of the present invention is to provide a
thermoplastic resin composition capable of the second molding for automotive
parts having high deep drawing such as instrument panel as well as calender
and extrusion molding.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a thermoplastic resin composition
capable for being used for skin materials of automotive interior parts
comprising:

20 (A) a base composition comprising (1) 5% to 45 % by weight, for
example 15% to 30% by weight, of a polypropylene; (2) 5% to 80 % by weight,
for example 40% to 60% by weight, of an olefin-base copolymer rubber; (3) 5%
to 30 % by weight, for example 10% to 20% by weight, of a processing oil; (4) 1%
to 30 % by weight, for example 5% to 20% by weight, of one chosen from low
25 density polyethylene resin, high density polyethylene resin and a mixture
thereof;

(B) 0.02-5 parts by weight, for example 1% to 3% by weight, of an
organic peroxide crosslinking agent on the basis of 100 parts by weight of the
base composition (A);

(C) 0.1-5 parts by weight, for example 1% to 3% by weight, of a crosslinking aid on the basis of 100 parts by weight of the base composition (A); and

5 (D) 0.5-5 parts by weight, for example 1% to 3% by weight, of a polytetrafluoroethylene on the basis of 100 parts by weight of the base composition (A).

The components of the thermoplastic resin composition of the present invention will be discussed in detail.

10 (A) Base composition

(1) Polypropylene resin

A polypropylene resin to be used in the present invention is an atactic polymer prepared as a block copolymer or random copolymer of propylene and α -olefin monomer. The polypropylene resin is a crystalline polymer having a
15 melt index (230°C, 2160 g) of from 0.1 to 60 g/10min, preferably 5 to 20 g/10min. If the fluidity is higher the range, the thermoplastic composition is inferior in calender molding due to lowered viscosity. Examples of α -olefin monomer include ethylene, propylene, 1-butene, 1-pentene, and 1-hexene.

Another polypropylene resin to be used in the present invention is an
20 organic peroxide prepared by extruder having a melt index (230°C, 2160 g) of 130-160 g/10min, preferably 140-150 g/10min.

The polypropylene resin of the present invention is used within the range of from 5 to 45 % by weight. If the content is less than 5 % by weight, the hardness and heat stability are lowered and emboss may not be formed during
25 vacuum thermoforming. On the other hand, if the content exceeds 45 % by weight, the sheets are easily bended and it is difficult to restoration due to too high hardness.

(2) Olefin-based copolymer rubber

An olefin-based copolymer rubber to be used in the present invention is amorphous and a random copolymer copolymerized with at least two monoolefins. A preferred representative of the olefin-base copolymer rubber is an ethylene-propylene-diene terpolymer copolymerized with ethylene and propylene as main components, that is, for example, where ethylene and propylene comprise at least 80% by weight of the copolymer rubber. It is also preferred to use dicyclopentadiene, 1,4-hexadiene, methylene norbornene, ethylidene norbornene, cyclohexadiene or its derivatives to allow unsaturated function in the terpolymer. Among terpolymers, an ethylene-propylene-ethylidene-norbornane is a preferred embodiment.

Besides the above olefin-base copolymer rubbers, other olefin-base copolymer rubbers may be used in the present invention and examples thereof include ethylene-propylene copolymers (EPM), ethylene-octene copolymers (EOM), ethylene-butene copolymers, and styrene-ethylene-butylene-styrene copolymers (SEBS). Among these, ethylene-propylene copolymers, ethylene-octene copolymers, and ethylene-butene copolymers are particularly preferred. A melt index (230°C, 2160 g) of the ethylene-propylene copolymers is 1 g/10min or less and melt indexes (230°C, 2160 g) of ethylene-octene copolymers and ethylene-butene copolymers are 5 g/10min or higher. A mixture of olefin-base copolymer rubbers may be used.

The olefin-base copolymer rubber of the present invention is used within the range of from 5 to 80 % by weight. If the content is less than 5 % by weight, the hardness is too high and thus sheet molding is not applicable. On the other hand, if the content exceeds 80 % by weight, the hardness is lowered and thus the heat stability is inferior.

(3) Processing oil

A processing oil to be used in the present invention is preferred to be a paraffin-type mineral oil having an ignition temperature of from 300 to 580 °C.

Conventional paraffin wax has excellent moldability but it has a problem in storage stability. However, the preferred processing oil when used in the present invention has been proved to improve both moldability and storage stability of the thermoplastic resin composition.

5 The processing oil of the present invention is used within the range of from 5 to 30 % by weight. If the content is less than 5 % by weight, the cost may increase and processability is inferior. On the other hand, if the content exceeds 30 % by weight, the storage stability is inferior at a high temperature, resulting in leakage on the surface of the sheet.

10 (4) Polyethylene resin

A polyethylene resin to be used in the present invention may be a low density polyethylene resin, a high density polyethylene resin or a mixture thereof.

15 The low density polyethylene resin used in the present invention is a copolymer of ethylene and α -olefin monomer and has a melt index (190°C, 2160 g) of 10 g/10min or less, preferably 1 g/10min or less. If the fluidity increases the above range, the appearance of molded articles is excellent but the resins have poor calender moldability and a low melt strength to deteriorate the
20 second moldability such as vacuum thermoforming, thus being inappropriate to use as automotive parts requiring deep drawing such as instrument panel. Examples of the α -olefin monomer include 1-butene, 1-pentene, and 1-hexene.

 The high density polyethylene resin used in the present invention is a copolymer of ethylene and α -olefin monomer and has a melt index (190°C, 2160
25 g) of 5 g/10min or less, preferably 1 g/10min or less. If the fluidity increases the above range, the appearance of molded articles is excellent but the emboss surviving ratio is decreased. Examples of the monomer include 1-butene, 1-pentene, and 1-hexene.

 The polyethylene resin of the present invention is used within the range

of from 1 to 30 % by weight on the basis of the base composition (A). If the content is less than 1 % by weight, it is not practical for the product requiring high deep drawing. On the other hand, if the content exceeds 30 % by weight, the heat stability is deteriorated.

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(B) Organic peroxide crosslinking agent

A crosslinking agent to be used in the present invention is organic peroxides, and specific examples include benzoyl peroxide, lauryl peroxide, dicumyl peroxide, 1,3-bis(*t*-butylperoxyisopropyl)benzene, di(*t*-butyl) peroxide, 10 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane, 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane-3, *n*-chlorobenzoyl peroxide, *n*-butyl-4,4-bis(*t*-butylperoxy) ballrate, 2,4-dichlorobenzoyl peroxide, or mixtures thereof. Among these, 1,3-bis(*t*-butylperoxyisopropyl)benzene is more preferred in the view of odor and scorch stability. An amount of the crosslinking agent may be adjusted depends 15 on the degree of crosslinking and flowability of the resin and is preferably used within the range of from 0.01 to 5 parts by weight on the basis of 100 parts by weight of the base composition (A) comprising the components (1)-(4). During the curing process with the organic peroxide, it is preferred to use after impregnation in a random polypropylene for homogeneous dispersion and 20 better molding process which can otherwise be problems with a small amount of peroxides used.

(C) Crosslinking aid

A crosslinking aid of the present invention is used to prevent hyper- 25 degradation of the polypropylene resin and stabilize radicals produced. An amount of the crosslinking aid is used within the range of from 0.01 to 5 parts by weight on the basis of 100 parts by weight of the base composition (A). Examples of the crosslinking aid include divinylbenzene, ethylene glycol dimethacrylate, triallyl cyanurate, diethylene glycol dimethacrylate, allyl

methacrylate, trimethylolpropane trimethacrylate. Among these, triallyl cyanurate is more preferred.

(D) Polytetrafluoroethylene resin

5 Besides the above components of the present invention, a fluorocarbon, particularly polytetrafluoroethylene resin may be used to improve the melt strength. It is used within the range of from 0.5 to 5 parts by weight on the basis of 100 parts by weight of the base composition (A). Polytetrafluoroethylene resin is well known as a tradename of "Teflon" such as
10 800J of Dupont Corp.

The components of the present composition may be compounded and coextruded through Bambury kneader, twin screw extruder, or buss kneader. However, since continuous processing may influence the quality of the final products, continuous extruding devices are preferred to batch devices. The
15 components of the present composition can be melt-kneaded by the use of single-, twin-screw extruder or buss kneader at 130-280 °C, preferably 190-250 °C, to obtain a sheeted item having desired properties and homogeneity.

Again, it may be desirable to premix the crosslinking agent, the crosslinking aid, or both in separate portions of the polyolefin to improve mixing
20 characteristics of these minor components.

The following examples are intended to further illustrate the present invention without limiting its scope. Testing methods employed in measuring properties in the Examples and Comparative Examples are as follows.

25 (1) Procedure for preparing Specimen : Sheetting was performed by a roll mill (roll size, 8 inches in diameter; and working temperature of 200 °C) and specimen was prepared to meet standard requirement.

(2) Property tests:

(1) Tensile strength and tensile elongation: Tested according to JIS K 6301 with a rate of 500 mm/min

(2) Roll mill moldability : Sheetting was performed by a roll mill at 200 °C and adhesion of the sheet was determined.

5 (3) Embossing survival ratio : A sheet having emboss surface was formed by vacuum thermoforming and the conditions of its surface were observed.

(4) Vacuum moldability : The sheet having an embossed surface was formed by vacuum thermoforming and the crack, torn condition, and thickness
10 changes in appearance were observed.

Further, each of components and abbreviation thereof used in Examples and Comparative Examples are as follows.

(1) PP-1 : Polypropylene resin having an ethylene content of 8 % and a melt index (230 °C, 2160 g) of 4 g/10min.

15 (2) PP-2 : Polypropylene resin having an ethylene content of 8 % and a melt index (230 °C, 2160 g) of 180 g/10min.

(3) PP-3 : Ethylene-propylene copolymer rubber, which is atactic polymer, having a melt index (230 °C, 2160 g) of 1.0 g/10min.

(4) EPM : Ethylene-propylene copolymer rubber having an ethylene
20 content of 72 % and a melt index (230 °C, 2160 g) of 0.7 g/10min.

(5) EPDM-1 : Ethylene-propylene-diene monomer copolymer rubber having a specific gravity of 0.86, an ethylene norbornene (ENB) content of 5 %, and a Mooney viscosity (ML₁₊₄ (125 °)) of 60 dL/g.

(6) EPDM-2 : Ethylene-propylene-diene monomer copolymer rubber
25 having a specific gravity of 0.86, an ethylene norbornene (ENB) content of 4.7 %, and a Mooney viscosity (ML₁₊₄ (125 °)) of 26 dL/g.

(7) Processing oil : WO-1900 of Michang Oil. Co., Ltd.

(8) EOR : Ethylene-octene copolymer rubber having a specific gravity of 0.86 and a melt index (190 °C, 2160 g) of 5 g/10min.

(9) LDPE : Low density polyethylene resin having a melt index of (190 °C, 2160 g) of 0.8 g/10min.

(10) HDPE : High density polyethylene resin having a melt index of (190 °C, 2160 g) of 0.7 g/10min.

5 (11) PTEF : Polytetrafluoroethylene (800 J of Dupont, Teflon™)

(12) Paraffin wax : LG-102N of Lion Chemicals.

(13) Organic peroxide : 1,3-bis(t-butyl)peroxideisopropyl benzene (Perkadox 14-40 of Akzo chemicals)

10 (14) Crosslinking aid : Triallylisocyanurate (Perkalink 301-40 of Akzo Chemicals)

Preparation Example : Preparation of polypropylene/olefin copolymer rubber

Preparation of TPE-1

15 EPDM-1 of 60 % by weight, PP-1 of 20 % by weight, and a processing oil of 20 % by weight were charged, and melt-kneaded at pre-heated Bambury mixer for 10 min and then pelletized.

Preparation of TPE-2

20 EPDM-2 of 60 % by weight, PP-1 of 20 % by weight, and a processing oil of 20 % by weight were charged, and melt-kneaded at pre-heated Bambury mixer for 10 min and then pelletized.

Preparation of TPE-3

25 EPDM-1 of 60 % by weight, PP-2 of 20 % by weight, and a processing oil of 20 % by weight were charged, and melt-kneaded at pre-heated Bambury mixer for 10 min and then pelletized.

Each content of components used for preparing olefin-base copolymer rubber pellets is described in Table 1.

Table 1

| Component | Content (% by weight) | | |
|----------------|-----------------------|-------|-------|
| | TPE-1 | TPE-2 | TPE-3 |
| EPDM-1 | 60 | | 60 |
| EPDM-2 | | 60 | |
| PP-1 | 20 | 20 | |
| PP-2 | | | 20 |
| Processing oil | 20 | 20 | 20 |

Examples 1-4

5 TPE-1, TPE-2, TPE-3, PP-1, EPM, LDPE, HDPE, organic peroxide (Perkadox 14-40), and a crosslinking aid (Perkalink 301-40) were blended in the ratios shown in Table 2. The mixture was kneaded at 200-240 °C by using twin-screw extruder to prepare a pellet. After that, sheeting was performed by a roll mill (roll size, 8 inches in diameter; and working temperature of 200 °C) to
10 prepare specimen. Physical properties of the obtained resin composition were tested and the result is shown in Table 2.

When ethylene-propylene-diene copolymer rubber having high viscosity and ethylene-propylene-diene copolymer rubber having low viscosity were mixed in an appropriate ratio and then the mixture was mixed further
15 with polytetrafluoroethylene resin as shown in Table 2, both sheet molding and vacuum molding were the most excellent.

Comparative Examples 1-3

Based on the compositions of Examples 1-3, an excess amount of low
20 density polyethylene was used in Comparative Example 1, an excess amount of

PP-1 was used in Comparative Example 2, and an ethylene α -olefin (EOR) was replaced instead of an ethylene-propylene copolymer rubber (EPM) of Example 3 and polytetrafluoroethane (PTFE) was not used in Comparative Example 3. Except the contents, the specimen of Comparative Examples 1-3 were prepared
5 according to the Examples 1-3.

From the results in Table 2, the thermoplastic resin composition of the present invention is excellent in hardness, tensile strength, roll adhesion, embo survival ratio and vacuum moldability. Especially, the thermoplastic resin composition of the present invention is excellent in the extrusion and calender
10 moldabilities, thus suitable for skin materials of automotive interior parts.

Table 2

| Category | | Example | | | | Comparative Example | | |
|----------------------|-----------------------|---------|-----|-----|-----|---------------------|-----|-----|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 |
| Base composition (g) | TPE-1 | 30 | 30 | 30 | | 30 | 60 | 30 |
| | TPE-2 | 20 | 15 | 20 | 20 | 20 | | 20 |
| | TPE-3 | | | | 30 | | | |
| | PP-1 | 20 | 20 | 20 | | 10 | 35 | 20 |
| | PP-2 | | | | 10 | | | |
| | PP-3 | | | | 10 | | | |
| | EPM | 15 | 10 | 15 | 15 | | | |
| | EOR | | | | | | | 15 |
| | LDPE | 10 | 15 | 10 | 15 | 35 | 5 | 10 |
| | HDPE | 5 | 10 | 5 | | 5 | | 5 |
| Additive (g) | Org. peroxide | 2 | 2 | 3 | 2 | 2 | 2 | 2 |
| | Crosslinking aid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| | PTFE | 3 | 3 | 3 | 3 | | | |
| | Paraffin wax | 3 | | | | | | |
| Physical property | Hardness | 93A | 96A | 96A | 93A | 88A | 97A | 94A |
| | Tensile strength | 105 | 107 | 110 | 100 | 94 | 115 | 100 |
| | Roll adhesion | - | ○ | ○ | - | ○ | ○ | |
| | Emboss survival ratio | | ○ | ○ | ○ | × | | |
| | Vacuum moldability | - | | | ○ | | × | ○ |

NOTE TO CLIENT- NEED THESE SYMBOLS DEFINED! XXXXX